the similar molybdenum(V) thiocyanate system.[16] The potentiometric measurements reported above also suggest that K_3 is numerically small.

Estimation of Iron as Thiocyanate.—The present results indicate the need to maintain a constant, high, thiocyanate concentration in any spectrophotometric method for the estimation of ferric ion by formation of thiocyanate complexes. The association constants of these complexes are not large and, as is apparent from Fig. 6, almost complete conversion to any one complex does not occur, even at high thiocyanate concentrations. Also, although ferric hydroxyl complex formation can be reduced to negligible proportions by using sufficiently acid solutions, ferric ion forms with many other anions complexes of stabilities comparable with, or exceeding, those with thiocyanate. Except under carefully controlled conditions such a method is, therefore, not likely to be capable of high precision. When greater accuracy is desired reduction to ferrous ion and the use of much more strongly complex-forming reagents such as α,α'-dipyridyl ion or *o*-phenanthroline appears to be preferable.

CANBERRA, AUSTRALIA

[16] D. D. Perrin, THIS JOURNAL, **80**, 3540 (1958).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BAYLOR UNIVERSITY]

Equilibrium Studies of the Copper(II) Oxalate Complex Between an Aqueous Solution and an Anion-exchange Resin[1]

BY LEONE D. COCKERELL AND PATRICK H. WOODS[2]

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The equilibrium of the copper(II) oxalate complex existing between an aqueous solution and an ion-exchange resin has been studied. The copper(II) bioxalate complex is stable on the resin, although it does not exist in a dilute aqueous solution. Evidence for a coördination number of six for copper(II) is given. A high *p*H and low oxalate in solution favor the uptake of copper(II) on an anion-exchange resin.

Introduction

The copper(II) oxalate complex has been investigated and its formula and stability constant in solutions of an oxalate salt determined. In 1936 Britton and Jarrett[3] in an electrometric investigation of the copper(II) oxalate complex in solutions of sodium oxalate showed the complex to have the formula $Cu(C_2O_4)_2^=$. This work has been confirmed several times, most recently by Meites[4] in 1950 by polarographic means. The purpose of the present work was to study the equilibrium of the copper(II) oxalate complex existing between an aqueous solution and an ion-exchange resin. The general approach used was that of Stokes and Walton[5] and/or Salmon.[6] The use of an ion-exchange resin previously saturated with the ligand is suggestive of Fronaeus[7] but his treatment was not applicable in this case. The metal ion concentration was much too high (7×10^{-2} *M*) and the existence of the uncharged complex could not be assumed. Instead, the data were plotted after the manner of Bjerrum.[8]

Experimental

Materials.—Reagent grade chemicals were used throughout the investigation except for primary standard sodium oxalate and potassium dichromate which were used for standardization purposes.

Amberlite IRA-401, a strongly basic quaternary ammonium type resin was used, because it has a low degree of cross-linkage which permits the exchange of large anions. The chloride form of the resin was converted to the oxalate form with concentrated solutions of sodium oxalate. It was washed until the effluent was free of the oxalate ion, backwashed, column dried and finally air dried before use. The moisture content, determined by drying at 110° for 3 hr., was 35.9%. The swollen volume (in water) of the air-dried resin was determined pycnometrically. The dry volume of the air-dried resin was determined by displacement of hexane.[9] The values are: swollen volume, 1.682 cc./g. of air-dried resin; dry volume, 0.888 cc./g. of air-dried resin; internal solution volume, 0.794 cc./g. of air-dried resin.

To obtain the ion capacity, a weighed quantity of the oxalate form of the resin was placed in sulfuric acid and the eluted oxalate ion was titrated with potassium permanganate. This value was checked by converting to the hydroxide form, adding excess nitric acid and back titrating with standard sodium hydroxide. The exchange capacity per gram of air dried resin was 1.150 meq./g.

Preparation of Solution.—The copper(II) oxalate complex solution used for equilibration was prepared by bringing solid copper oxalate (J. T. Baker Analyzed >99.5%) into solution with sodium oxalate. Standardization was done by potassium permanganate for the oxalate and iodometrically for the copper.

Equilibration Technique.—One gram (1.150 meq.) of the oxalate resin was placed in a 130-ml. polyethylene bottle with a measured volume of the solution containing the complex and free sodium oxalate. Water was added to make a total of 100 ml. of solution. This was agitated at 30° for 18 hr. Preliminary runs had shown that equilibrium was attained shortly after 12 hr.

Analytical.—Copper content, total oxalate and *p*H were determined on the solution after equilibration. The *p*H was measured with a Beckman Model G meter. Copper and oxalate were determined as in the original analysis of the solution containing the complex. The analysis of the resin was done by difference since all ionic species were known. No attempt was made to correct for activities as available constants are not thermodynamic ones. No attempt was made to maintain constant ionic strength because this would have required addition of another salt whose anions would have entered the resin and caused unnecessary complications.[10]

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[1] Presented at the Eleventh Southwest Regional Meeting of the American Chemical Society at Houston, Texas, December 1, 1955.

[2] Taken from a thesis presented by Patrick H. Woods in partial fulfillment of requirements for the Doctor of Philosophy degree.

[3] H. T. S. Britton and M. E. D. Jarrett, *J. Chem. Soc.*, 1489 (1936).

[4] L. Meites, THIS JOURNAL, **72**, 184 (1950).

[5] Ruth H. Stokes and H. F. Walton, *ibid.*, **76**, 3327 (1954).

[6] J. E. Salmon, *Revs. Pure and Appl. Chem.*, **6**, 24 (1956).

[7] S. Fronaeus, *Svensk Kem. Tidskr.*, **65**, 1 (1953).

[8] J. Bjerrum, "Metal-Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[9] H. F. Walton, *J. Phys. Chem.*, **47**, 371 (1943).

[10] S. Fronaeus, *Acta Chem. Scand.*, **8**, 1174 (1954).

TABLE I

EQUILIBRATION OF 1.150 MEQ. OF IRA-401 IN THE OXALATE CYCLE WITH 0.700 MMOLE OF COPPER(II) AND VARYING OXALATE IN 100 ML. OF SOLUTION

Taken at pH 7.00	Soln. after				Resin after (by difference)		Distribution of resin oxalate for electroneutrality		Ratio
Mmole oxalate total system	pH	Mmole Cu^{++}	Mmole $C_2O_4^-$ total	Mmole $C_2O_4^-$ free[a]	Mmole oxalate total	Mmole Cu^{++}	Mmole of $C_2O_4^=$ probably distributed between $Resin^+$ and Cu^{++}	Mmole $HC_2O_4^-$ bound to Cu^{++}	Mmole $HC_2O_4^-$ Mmole Cu^{++}
2.919	8.77	0.179	1.245	0.887	1.674	0.521	0.518	1.156	2.22
5.493	8.79	.278	3.912	3.256	1.581	.422	.413	1.168	2.77
8.067	8.80	.357	6.563	5.848	1.504	.343	.332	1.172	3.42
10.443	8.73	.387	8.981	8.206	1.462	.313	.314	1.148	3.67
13.017	8.74	.417	11.623	10.790	1.394	.283	.322	1.072	3.79
16.371	8.76	.446	14.998	14.207	1.373	.254	.285	1.088	4.28
18.158	8.74	.471	16.793	15.851	1.365	.229	.243	1.122	4.90
Taken at pH 9.00									
3.075	9.02	0.159	1.391	1.073	1.684	0.541	0.548	1.136	2.10
5.575	9.05	.258	3.975	3.459	1.600	.442	.434	1.166	2.64
8.075	9.00	.318	6.573	5.937	1.502	.382	.412	1.090	2.85
10.575	8.94	.385	9.175	8,405	1.400	.315	.380	1.020	3.24
13.075	8.93	.412	11.690	10.866	1.385	.288	.341	1.044	3.63
15.575	8.90	.437	14.182	13.308	1.393	.263	.283	1.110	4.22
18.075	8.80	.468	16.685	15.749	1.390	.232	.224	1.166	5.03
20.575	8.85	.489	19.197	18.219	1.378	.211	.194	1.184	5.60

[a] Based on a value of $10^{8.3}$ for the stability constant of the $Cu(C_2O_4)_2^=$ complex.

Donnan effects could be neglected because the volume of internal solution in the resin was small compared to the total volume.[11] The resin was ashed, extracted with water and tested for the sodium ion with standard acid. A maximum of 0.03 meq. of sodium ion was absorbed at high oxalate concentration.

Results and Treatment of Data

Preliminary Experiments.—Working under the assumption that the complex ion on the resin would have the formula $Cu(C_2O_4)_2^=$, the same as that in solution, the copper was varied, oxalate was held constant, and pH determined although no attempt was made to control it. After the equilibration the analysis of the solution showed that the oxalate on the resin exceeded that which would be expected on the basis of the formula $Cu(C_2O_4)_2^=$ and that the total negative charge was greater than the ion capacity of the resin. It was concluded that bioxalate had entered the resin phase as part of the copper(II) complex, since the ashed resin yielded only a trace of sodium ion and furthermore it had been shown that the resin would not take up bioxalate at pH 7 in the absence of copper(II).

Experimental Work at Constant pH and Copper(II) Concentration.—To limit all variables except one, the work was done at a constant copper(II) concentration and at a constant pH. The millimoles of oxalate used varied from about 2.5 to 20 mmoles per 100 ml. of solution. Runs at pH of 7.00 and 9.00 were taken.

The data obtained are given in Table I. The solution data were obtained by direct analysis of solution, and the resin data by difference. The resin data gave only total oxalate and copper(II) known to be on the resin. The oxalate content was then distributed between bioxalate bound to copper(II) and oxalate presumably bound partially to both copper(II) and resin$^+$. This was done to conserve both oxalate and electroneutrality of the resin.

The method of calculation is shown using resin data taken from the bottom of Table I for pH of 7.00

$$\text{Mmole } HC_2O_4^- = 2(\text{mmole total oxalate in resin}) - \{(\text{mmole resin}^+ + 2(\text{mmole Cu}^{++})\}$$

$$\text{Mmole } HC_2O_4^- = 2(1.365) - \{1.150 + 2(0.229)\} = 1.122$$

$$\text{Mmole } C_2O_4^= \text{ (as such)} = \text{mmole total oxalate in resin} - \text{mmole } H_2O_4^-$$

$$\text{Mmole } C_2O_4^= \text{ (as such)} = 1.365 - 1.122 = 0.243$$

The bioxalate/copper(II) ratios were plotted against the negative logarithm of the free oxalate in solution after the manner of Bjerrum[8] to obtain a portion of the formation curve of the copper(II) bioxalate complex. Only the bioxalate/copper(II) ratio was plotted since other ligands, water and/or oxalate cannot be fixed from the experimental data available.

Discussion

Copper(II) on the Resin.—A low concentration of free oxalate in solution and a high pH favor the uptake of copper(II) on the resin (Fig. 1). An increase in oxalate results in the gradual elution of the complex from the resin.

The Formation of the Bioxalate Complex (Fig. 2).—Only the top portion of the curve was available because a lower oxalate concentration in solution resulted in the precipitation of copper oxalate. Copper(II) probably coördinates six bioxalates since 5.6 were determined experimentally. The final attainment of six was impossible because of

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[11] H. P. Gregor, THIS JOURNAL, **73**, 642 (1951).

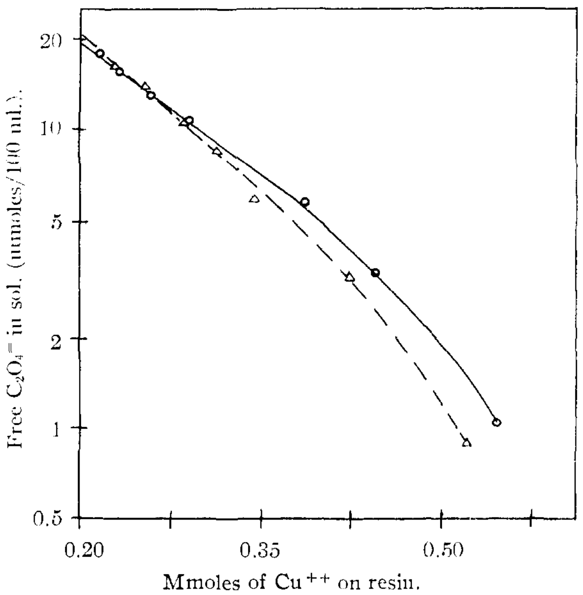

Fig. 1.—O, *p*H 9.00; △, *p*H 7.00.

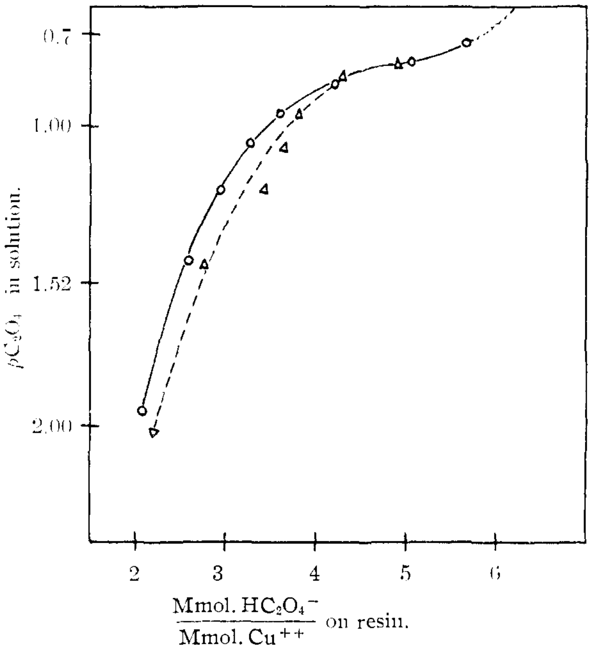

Fig. 2.—O, *p*H 9.00; △, *p*H 7.00.

the limited solubility of sodium oxalate in water. No attempt was made to determine the magnitude of the complexity constant because the exact amount of oxalate in the complex cannot be determined. It appears that the complex starts as $Cu(C_2O_4)_2^=$ and that the bioxalate displaces oxalate, then adds more, until eventually the complex of formula $Cu(HC_2O_4)_6^{-4}$ is produced. Whereas this anion would not be stable in solution due to electrostatic repulsions, our data indicate that it is stabilized by the resin. Since a resin has a relatively high concentration of positive charges, it can exert a screening effect which will favor and stabilize a more highly charged anion.

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WACO, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

Sexadentate Chelate Compounds.[1] X

BY FRANCIS LIONS AND KENNETH V. MARTIN[2]

RECEIVED DECEMBER 23, 1957

A number of new linear sexadentate chelate compounds and some related tridentate and quadridentate chelate compounds have been prepared and some of their coördination compounds studied. One of them—the α-pyridyl-hydrazone of pyridine-2-aldehyde—appears to be a promising reagent for the colorimetric estimation of cobalt.

In the simplest type of sexadentate chelate molecule, the six donor atoms are located successively along a chain, which, when coördination takes place, becomes wound round the coördinated metal atom in such a way as to bring the six donor atoms into positions at the apices of the coördination octahedron. The final position taken up by the chelating residue must be relatively strainless. Certain of the structural details requisite for the successful design of such molecules have been reported previously.[3] In this paper further experiments are described which also bear on this question of design.

It was pointed out in Part V of this series of papers[3] that it should be possible to substitute for the two sulfur atoms of 1,8-diamino-3,6-dithiaoctane (EEE base) two >N–CH_3 groups, which, despite the tertiary nature of the nitrogen atoms, might well be expected to function as donor atoms and thus enable 1,8-bis-(salicylideneamino)-3,6-dimethyl-3,6-diazaoctane to behave as a sexadentate chelate compound. It was considered at the time that the formation of imidazolidine rings

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(1) The term "chelate compound" as used by the authors conforms to the original definition given by G. T. Morgan and H. D. K. Drew (*J. Chem. Soc.*, **117**, 1457 (1920), footnote) in the words "The adjective "chelate" derived from the great claw or "chela" (chely) of the lobster and other crustaceans, is suggested for *these caliper-like groups* which function as two associating units and fasten on to the central metallic atom so as to produce heterocyclic rings." Some chemists today regard the actual final coördination compound as the chelate compound. In our opinion this is wrong. We would define a chelate compound as a compound "whose molecule is capable of attaching itself either directly or after loss of a proton or protons to a suitable metal atom at more than one point."

(2) University Research Grant Student of the University of Sydney.

(3) *Cf.* F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, THIS JOURNAL, **74**, 4188 (1952); **75**, 1526, 2443 (1953); **76**, 383 (1954).